

E-Content Study Material

B. Sc. Chemistry (H)

2nd Year

Paper II B

Inorganic Chemistry

Chapter VIII: Non-aqueous Solvents

Topic: Reactions in Liquid SO₂

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Liquid Sulphur Dioxide

Liquid sulphur dioxide is also a non-protonic solvent as it does not yield a proton (H^+) on ionization. It is widely used for carrying out a number of chemical reactions.

Under normal temperature and pressure, sulphur dioxide is a gas but it can be readily liquefied. It has a wide liquid range ($-10^{\circ}C$ to $-75.5^{\circ}C$) and hence can serve as a good solvent. Its use as a non-aqueous solvent is rapidly increasing due to its low cost and ease of its handling. Its dielectric constant is small (17.4 at $-20.0^{\circ}C$) which makes it a good solvent for electrovalent compounds.

The characteristic physical properties of liquid sulphur dioxide are given in Table.

Table: Physical Properties of Liquid Sulphur Dioxide.

Properties	Values
Boiling point	-10.1°C
Freezing point	-75.5°C
Density	1.46 g ml ⁻¹ (-10°C)
Dielectric constant	17.4 (-20°C)
Specific conductance (ohm ⁻¹ cm ⁻¹)	4x10 ⁻⁸ (-10°C)
Viscosity (centipoise)	0.428 (-10°C)
Dipole moment (Debye)	1.61

Autoionisation.

By analogy with water and liquid ammonia, autoionisation of sulphur dioxide takes place as under:



The thionyl ion (SO²⁺) is analogous to the hydronium ion (H₃O⁺) and ammonium ion (NH₄⁺) while sulphite ion (SO₃²⁻) corresponds to hydroxyl ion (OH⁻) and amide ion NH₂⁻ of the aqueous and liquid ammonia systems, respectively.

Sulphur dioxide solutions are not as good electrical conductors as are liquid ammonia or aqueous solutions.

Solubility of Substances in Liquid Sulphur Dioxide.

Amongst the inorganic compounds, iodides and thiocyanates

are the most soluble. Metal sulphates, sulphides, oxides and hydroxides are practically insoluble.

Many of the ammonium, thallium and mercuric salts are soluble. Liquid sulphur dioxide is an excellent solvent for covalent compounds. Substances such as IBr, PBr₃, CCl₄, SiCl₄, SnCl₄ are soluble in it. Metals are insoluble in liquid sulphur dioxide.

Amongst the organic compounds, benzene and alkenes dissolve in it freely. Pyridine, quinoline, ethers, halogen derivatives and acid chlorides also dissolve in liquid sulphur dioxide. Alkanes are insoluble.

Reactions in Liquid Sulphur Dioxide. Chemical reactions that occur in liquid sulphur dioxide are of the following types:

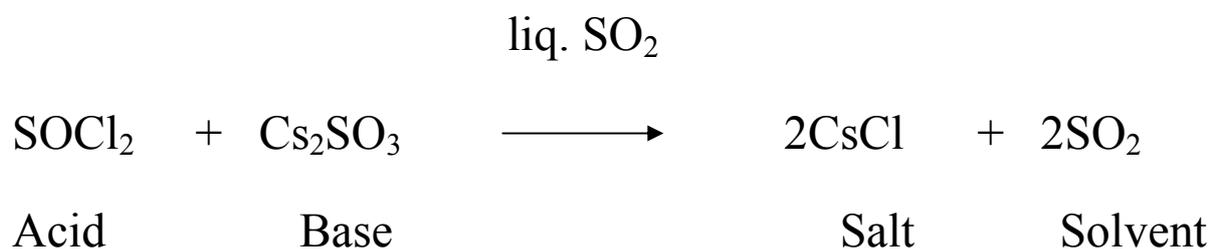
1. Acid-base Reactions or Neutralisation Reactions.

Comparing the autoionisation of liquid sulphur dioxide with that of water, it can be seen that thionyl ion (SO²⁺) is analogous to hydronium ion and sulphite ion (SO₃²⁻) is analogous to hydroxyl ion (OH⁻). Hence, all compounds containing or making available SO₃²⁻ ions in liquid sulphur dioxide will act as bases in this medium. Similarly, all compounds which make

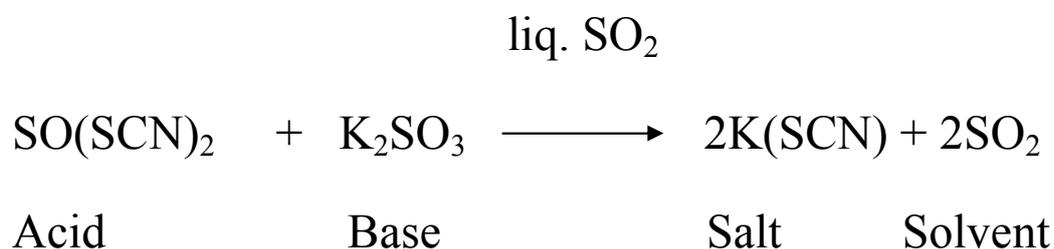
available SO^{2+} ions in liquid sulphur dioxide will act as typical acids in liquid sulphur dioxide.

Typical acid-base or neutralisation reactions in liquid sulphur dioxide are given below.

Reaction between thionyl chloride and cesium sulphite:

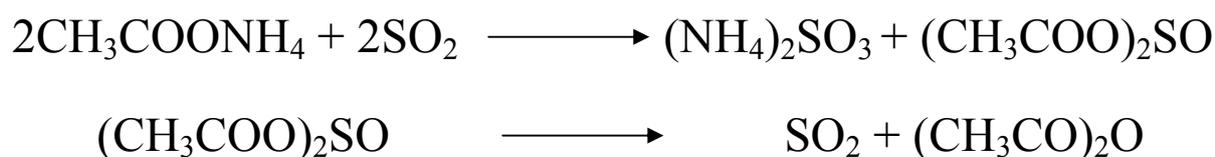


Reaction between thionyl thiocyanate and potassium sulphite.

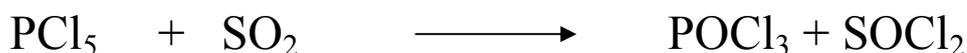


2. **Solvolytic Reactions.** Only a limited number of salts undergo solvolysis in liquid sulphur dioxide. Some common reactions are given below.

Ammonium acetate is solvolysed in liquid sulphur dioxide.

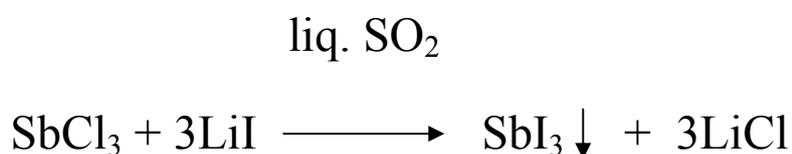
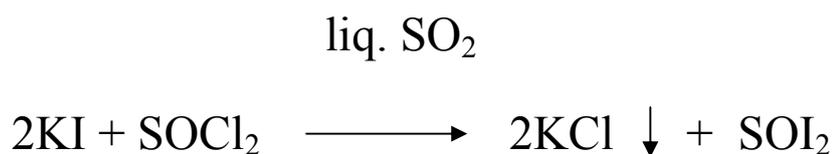
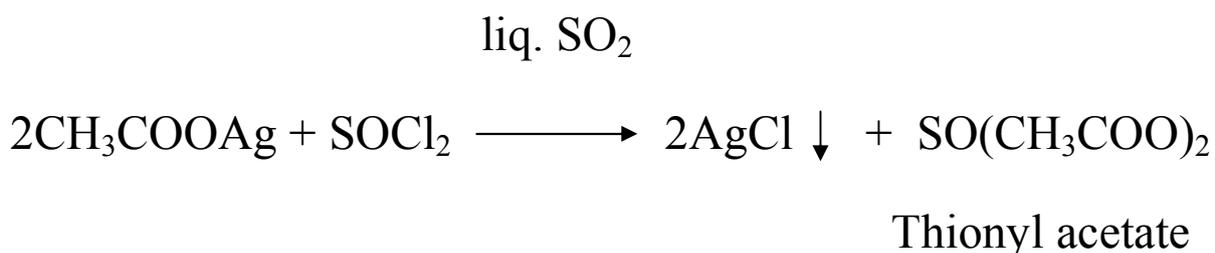


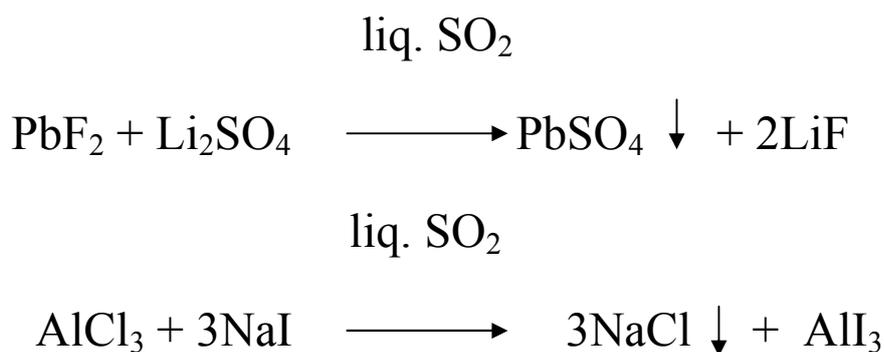
Binary halides such as PCl_5 , UCl_6 , WCl_6 undergo solvolysis in liquid sulphur dioxide.



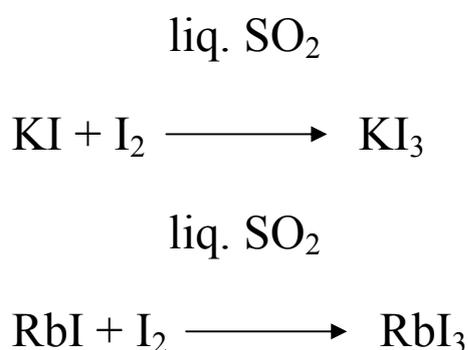
The formation of solvates, i.e., the addition compounds with the solvent, is also known. Typical solvates formed are $\text{NaI} \cdot 4\text{SO}_2$, $\text{RbI} \cdot 4\text{SO}_2$, $\text{KBr} \cdot 4\text{SO}_2$, $\text{CaI}_2 \cdot 4\text{SO}_2$, $\text{BaI}_2 \cdot 4\text{SO}_2$, $\text{SrI}_2 \cdot 4\text{SO}_2$, $\text{AlCl}_3 \cdot 2\text{SO}_2$, etc.

3. Precipitation Reactions. A large number of precipitation reactions can be carried out in liquid sulphur dioxide due to specific solubility relationships. Some of these reactions are given below.

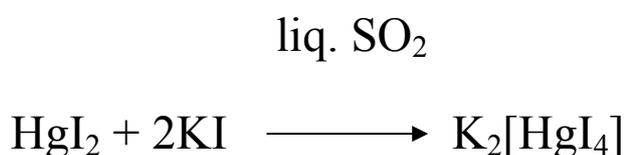




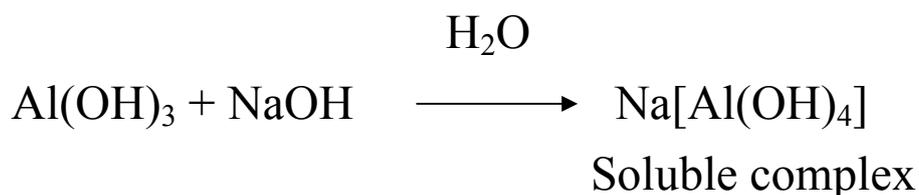
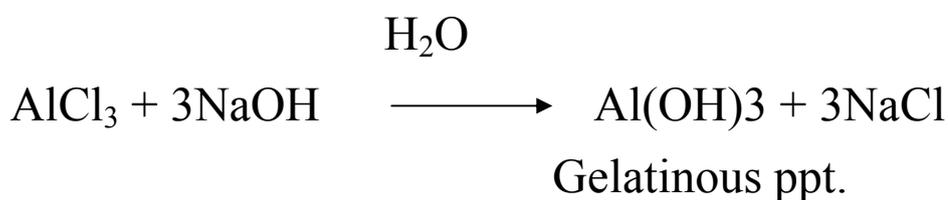
4. Complex Formation Reactions. A large number of complex formation reactions of liquid sulphur dioxide have been reported. For instance, the solubility of iodine in liquid sulphur dioxide is greatly increased by the addition of potassium or rubidium iodide. This is due to the formation of the complex KI_3 or RbI_3 .



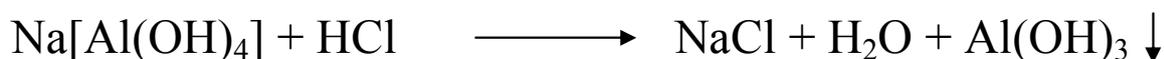
Similarly, the increase in the solubility of cadmium iodide and mercuric iodide in liquid sulphur dioxide is attributed to the formation of complexes.



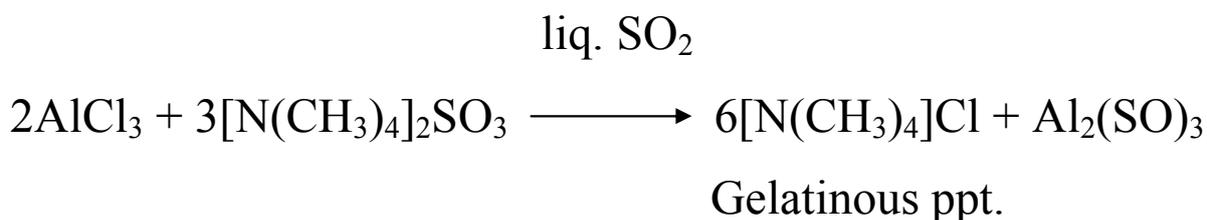
5. **Amphoteric Behaviour.** Various salts show amphoteric behaviour in liquid sulphur dioxide. The reaction of AlCl_3 with NaOH in aqueous medium can be compared with the reaction of AlCl_3 with tetramethyl ammonium sulphite in liquid sulphur dioxide. In aqueous solution, the reaction takes place as follows.

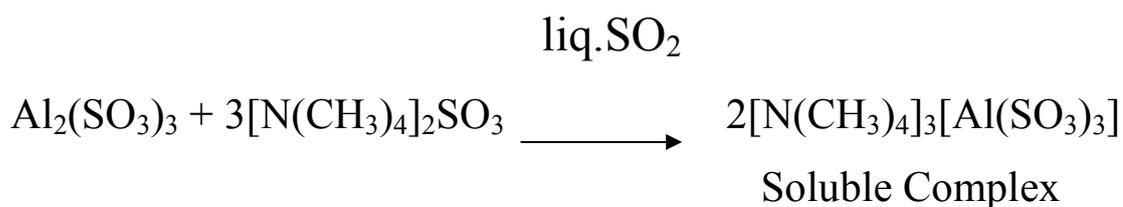


From the soluble complex, Al(OH)_3 can be reprecipitated by the addition of HCl .



In liquid sulphur dioxide medium, an identical reaction takes place between AlCl_3 and tetramethyl ammonium sulphite:



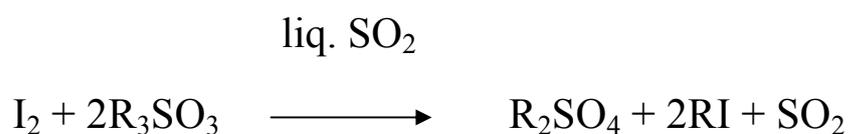


From the soluble complex, $\text{Al}_2(\text{SO}_3)_3$ can be reprecipitated by adding the acid, SOCl_2 .



The behaviour of GaCl_3 is similar to that of AlCl_3 .

6. Redox Reactions. Liquid sulphur dioxide does not have any strong oxidising or reducing properties. It serves only as a medium for redox reactions. For instance, liquid sulphur dioxide cannot reduce iodine. However, a sulphite in liquid sulphur dioxide reduces iodine to iodide.



KI is oxidised to free iodine by SbCl_5 in liquid sulphur dioxide.

